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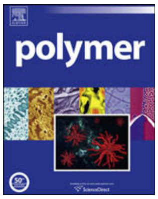

A density functional theory study of the mechanisms of scandium-alkoxide initiated coordination–insertion ring-opening polymerization of cyclic esters

Jun Ling [a,b,*], Jingguo Shen [b], Thieo E. Hogen-Esch [b]

[a] Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China
[b] Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA

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ABSTRACT

The generally accepted coordination–insertion mechanisms of scandium-alkoxide initiated ring-opening polymerizations of ε-caprolactone (CL), trimethylene carbonate (TMC) and (*S*,*S*)-lactide (LLA) were investigated using density functional theory calculations. The geometries and corresponding energies of four key proposed intermediates were evaluated and found consistent with these structures. The transition states corresponding to monomer addition indicate a penta-coordinate scandium and have nearly the same energies for all monomers. Thus CL, TMC and LLA undergo similar processes with relatively small differences in the energies of Sc-monomer coordination but the pre-transition state complex of TMC is much lower in energy than that of the other monomers. The dipole moments of the intermediates close to the transition states and the transition states themselves in all cases are lower than those of the reactants predicting faster reaction rates in low polarity solvents, consistent with experimental results. This study may be applicable to ring-opening polymerizations mediated by yttrium and other rare earth complexes.

1. Introduction

Ring-opening polymerizations (ROPs) of heterocyclic monomers, for instance, lactides, lactones and aliphatic cyclic carbonates, give polyesters and polycarbonates and have been studied for decades [1–6]. Examples include ε-caprolactone (CL), trimethylene carbonate (TMC) and (*S*,*S*)-lactide (LLA) whose structures are shown in Scheme 1. Many of these polymers have medical applications because of their good bio-compatibility and low toxicity and are typically biodegradable as well. The LLA, a dimer of L-lactic acid that is readily available from plants, is a sugar metabolism intermediate. The ROP of LLA is of both scientific and commercial importance because the PLLA polymer is a widely used biodegradable plastic with medical and other applications.

Alkali- and multivalent metal alkoxides (or compounds that convert into alkoxides upon initiation, such as phenolates, thiophenolates, amidates, imidates, etc.) have been reported as ROP catalysts [1–3]. These include complexes of tin [2,3,7–11], aluminum [2,3,12–15], zinc [2,3,16–19], magnesium [2,3,20,21], titanium [3,22–24], iron [25,26], scandium [3,10,11,27–31], yttrium [3,29,30,32–39], and lanthanides [3,29,32,34,35,40–59]. Among them, lanthanide, yttrium and scandium initiator complexes have been found to possess high catalytic activities (low residual catalyst) [60] as well as ease of removal [61]. Their low toxicities [61–63] and high activities at ambient temperature make them especially interesting for the synthesis of biocompatible materials.

Several types of ROP processes have been proposed for some of these catalysts, with mechanisms ranging from electrophilic to nucleophilic [1,3]. Proton activation and alkyl-oxygen bond heterolysis give rise to a cyclic monomer cation (cationic mechanism) [31,64]. Typical nucleophilic type catalysts for coordination–insertion mechanism polymerization are metal alkoxides, phenolates, thiophenolates, amidates, imidates, etc. that convert active centers into alkoxides upon initiation. First reported by Teyssié, Jérôme and Kricheldorf [65–68], coordination–insertion ring-opening mechanism was proposed to proceed through monomer coordination to the metallic center followed by monomer insertion into metal-chain end bond via acyl-oxygen cleavage [27,32,35,38,40,43,45–47,50,51,54]. Similar mechanisms have been postulated for metal alkoxides and derived phenolates including those of Sn [1,7–9], Al [1,3,13], Zn [16,17], Mg [2,20], Ti [22,24] and Fe [3,25] compounds. Only a few computational studies on the coordination–insertion ROP mechanism containing nucleophilic growing site of Mg-, Sn- and Al-initiator have been attempted [20,21,69–71].

For lanthanide, yttrium and scandium initiators, the experimental results are consistent with: (1) acyl-oxygen cleavage of

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* Corresponding author. Tel.: +86 571 87953739; fax: +86 571 87951773.
E-mail address: lingjun@zju.edu.cn (J. Ling).

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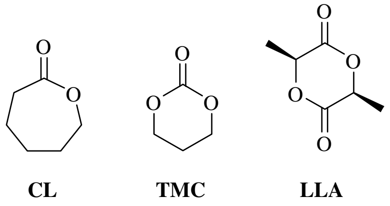


Scheme 1. Monomers.

monomer which results in polymers having hydroxy-alkyl end groups; (2) the propagation at the metal site of the growing chain; (3) the monomer coordination at the active site (plausibly ion pairs) [35,37,68]. Scheme 2 illustrates a typical coordination–insertion mechanism [35,37,68] for the case of a trivalent scandium active center that includes four steps: ***a***. coordination of the monomer carbonyl onto the metal ion giving electrophilic activation of the carbonyl carbon; ***b***. nucleophilic addition of the Sc alkoxide to the carbonyl group to give a bicyclic complex; ***c***. intramolecular alkoxide equilibrium exchange; and ***d***. ring opening by acyl-oxygen bond cleavage. Monomer coordination to Sc ion (step ***e***) starts a new cycle. However, to the best of our knowledge, no discrete intermediates appear to have been demonstrated.

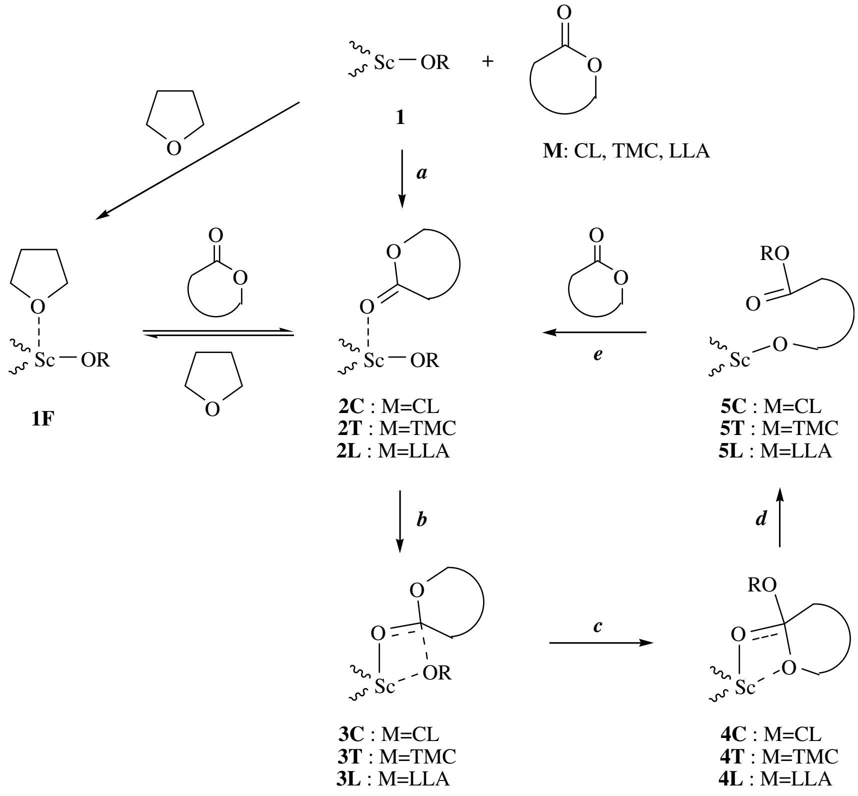
Herein we report in greater detail the analysis of the ROP initiation/polymerization mechanisms in the presence of scandium complexes, including the geometries and energies of the proposed reaction intermediates, based on density functional theory (DFT) studies. These computations provide further evidence for the intermediates shown in Scheme 2 and suggest a unique pentacoordinated Sc transition state involved in the conversion of **3** into **4**. Yttrium and other rare earth complexes may react via similar mechanisms because of their similarity to that of scandium.

2. Methods

Geometry optimizations were carried out by using DFT at the B3LYP/6-31G* level [72–74] that was recently shown to be sufficient for many cases [75–77]. Zero point vibrational energies (ZPE) were evaluated at B3LYP/6-31G*//B3LYP/6-31G* level. The vibrational frequency calculations were scaled by a factor of 0.98 [78]. All **M**, **1**, **1F**, **2**, **3**, **4**, **5** and **6** intermediates were characterized as minima (number of imaginary frequencies = 0) while **tsC**, **tsT** and **tsL** were transition states (number of imaginary frequencies = 1). Single point energies (SPE) were carried out at the B3LYP/6-311 + G** level and the final enthalpies were obtained as the sum of SPE and ZPE calculations. Atomic charges were calculated by natural bond orbital (NBO) analysis. All calculations were conducted with the Gaussian 03 program [79].

3. Results and discussion

The Sc methoxide mediated ROP coordination–insertion mechanisms for monomers of ε-caprolactone (CL), trimethylene carbonate (TMC) and (*S*,*S*)-lactide (LLA) were evaluated by B3LYP/6-31G* DFT methods. The corresponding optimized structure of $Sc(OC_6H_2\text{-}2,6\text{-}Bu^t\text{-}4\text{-}Me)_3$ indicates an approximately trigonal planar ScO_3 skeleton with Sc slightly above the plane of the three oxygens by 0.168 Å (Fig. S1 in Supporting Information) with an average Sc–O lengths of 1.900 Å, and O–Sc–O and Sc–O–C bond angles of 119.2° and 172.7° respectively. This agrees rather well with the reported X-ray data with corresponding measurements of 0.13 Å, 1.869 Å, 119.5° and 168.4°, respectively [80]. Since $Sc(O^iPr)_3$, $Sc(OMe)_3$ and $Sc(OMe)_2CL$ all have such similar structures (Fig. S2 in Supporting Information) we choose $Sc(OMe)_3$ as the simplest model compound for both the initiator and the active polymer chain with $Sc–O–CH_2$ active sites.



Scheme 2. Coordination–insertion mechanism of ring-opening polymerization of cyclic monomers.

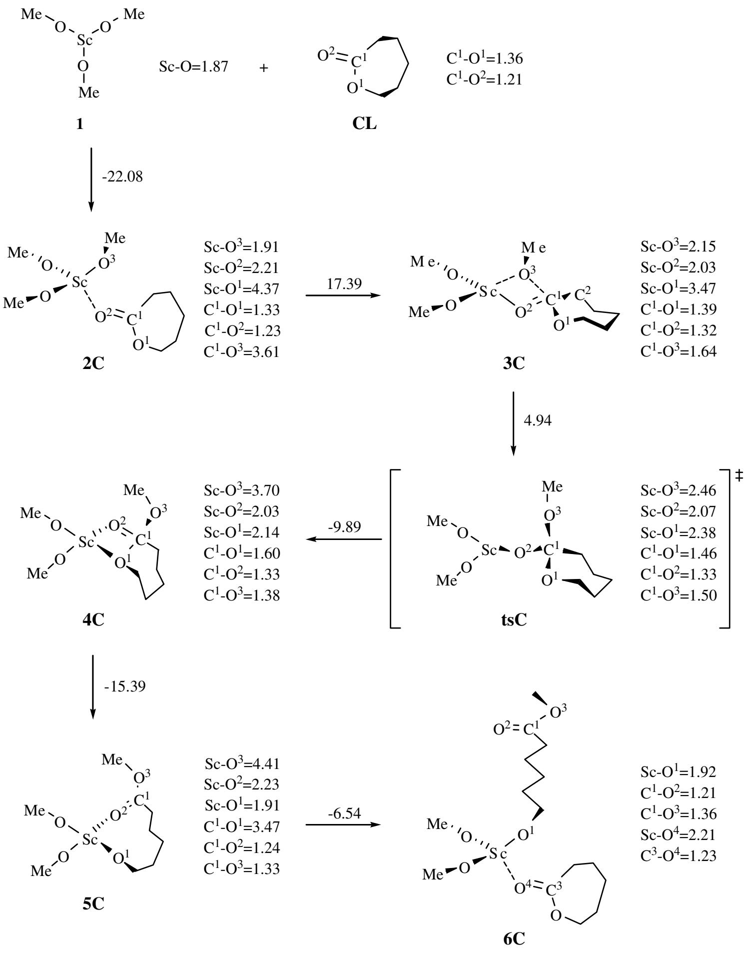


Fig. 1. ROP mechanism of CL. Bond lengths are in Å and energies in kcal/mol.

Fig. 1 and Fig. S3 show the DFT based energies for the ROP of CL and optimized geometries of the proposed intermediates. The *exo*-carbonyl group of CL coordinates the Sc metal (**2C**) with the O^1 in the “trans” position, resulting in a Sc–O^2 distance of 2.21 Å. The O^2–C^1–O^1 plane is almost vertical to the plane formed by the three methoxy oxygens. The C^1–O^2 and Sc–O^3 bonds give a dihedral angle of 11.2° (Fig. 1 and Fig. S3). A similar DFT based geometry was reported for the $SnMe_3OMe$ initiated 1,5-dioxepan-2-one (DXO) system [69]. However, the energy of coordination between $Sc(OMe)_3$ and CL is −22.08 kcal/mol, much larger than the $SnMe_3OMe$–DXO complex (−5.8 kcal/mol) consistent with the much longer distance between Sn and carbonyl oxygen (3.49 Å).

The transformation of **2C** into **3C** involves addition of the Sc–O^3 onto the C^1–O^2 double bond and a corresponding rotation of the O^1–C^1–O^2 plane of about 90° forming a planar four-membered ring (**3C**) having a sp^2–sp^3 hybridized C^1 which is located above the O^2–O^1–C^2 plane. This process lengthens the Sc–O^3 and shortens the Sc–O^2 bond (Fig. 1 and Fig. S3). This process requires considerable energy (17.39 kcal/mol). The natural bond orbital (NBO) charges on Sc and C^1 decrease and those on O^2 and O^3 increase (Fig. 2).

The conversion of **3C** to **4C** involves rotation of the CL ring around the C^1–O^2 bond resulting in a decrease and increase in the Sc–O^1 and Sc–O^3 distances respectively (Fig. 1). The calculated transition state, **tsC**, shows a *penta-coordinate* Sc with nearly equal Sc–O^1 and Sc–O^3 distances and a sp^3 hybridized C^1 atom with the C^1–O^1, C^1–O^2 and C^1–O^3 bond lengths between 1.33 and 1.50 Å. The **TS** energy is 4.94 kcal/mol above that of **3C**. The TS structure is supported by a DFT imaginary frequency check and an intrinsic reaction coordinate (IRC) calculation (Fig. S4 and a Video clip in Supporting Information) and differs from that proposed for the $SnMe_3OMe$/DXO system having a Sn-containing four-membered ring (see below) [69]. This may be due to the coordinative stability of the tetravalent Sn while Sc has the potential for an increased coordinating number [27,29,30].

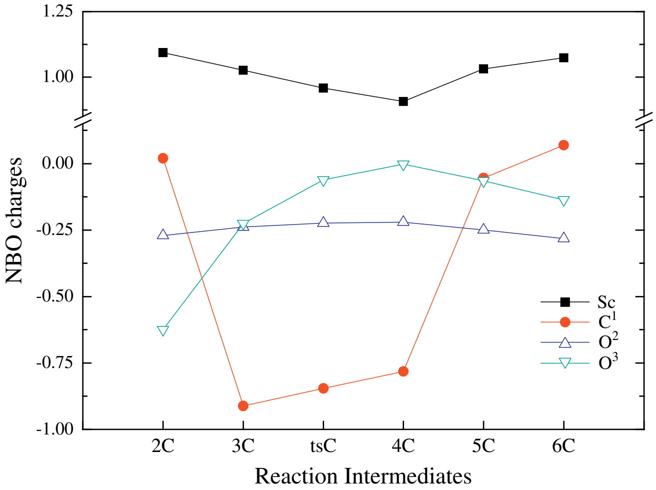


Fig. 2. Natural bond orbital charges of several atoms involved in the reaction intermediates in the polymerization of CL.

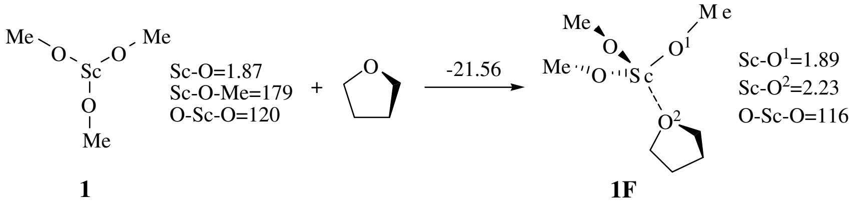


Fig. 3. Coordination of THF onto Sc(OMe)$_3$. The bond length and the energy are in Å and kcal/mol, respectively.

It is worth pointing out that, except for the formation of **2C** and **6C**, the Sc-mediated coordination–insertion mechanism differs from the reported Sn- and Al-mediated mechanisms [69,70]. In our case a single transition state, **tsC**, containing an *endo*-ring sp^3-hybridized C^1 is proposed. The Sn- and Al-mediated mechanisms are proposed involving two four-membered cyclic transition states separated by a stable intermediate implying that it may be possible to isolate such an intermediate.

As shown in Fig. 1, the conversion of **4C** into **5C** involves a C^1–O^1 bond cleavage that results in the recovery of the full C^1–O^2 carbonyl bond (C^1–O^2 = 1.24 Å) which remains strongly coordinated to the Sc center (Sc–O^2 = 2.23 Å) whereas the Sc–O^3 and C^1–O^1 distances increase significantly. The subsequent conversion of **5C** into **6C** involves the coordination to Sc of a new monomer that displaces the Sc–O^2 bond with an energy change of −6.54 kcal/mol. The overall energy change of the CL addition (energy between **2C** and **6C**) is −9.49 kcal/mol.

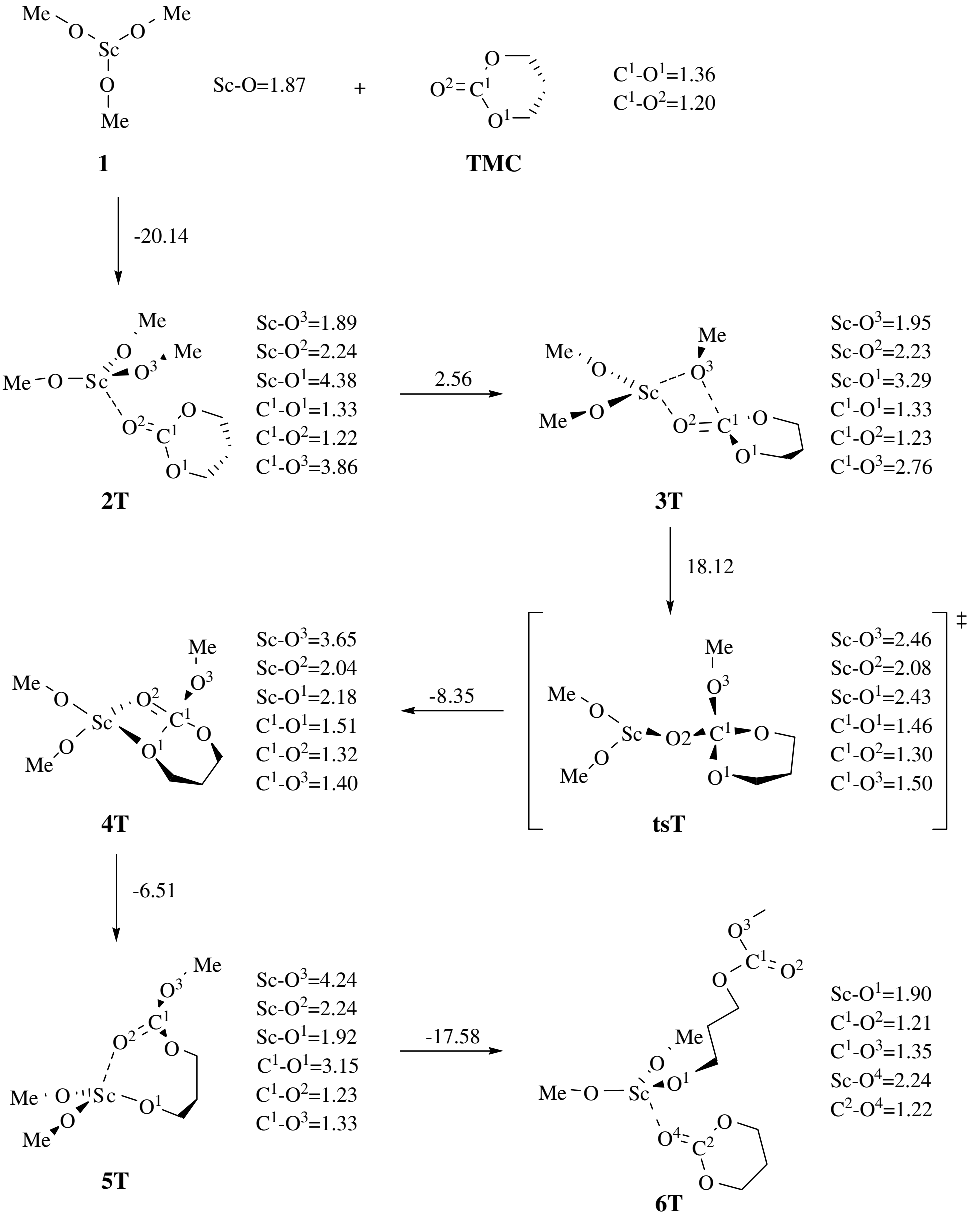


Fig. 4. ROP mechanism of TMC. Bond lengths are in Å and energies in kcal/mol.

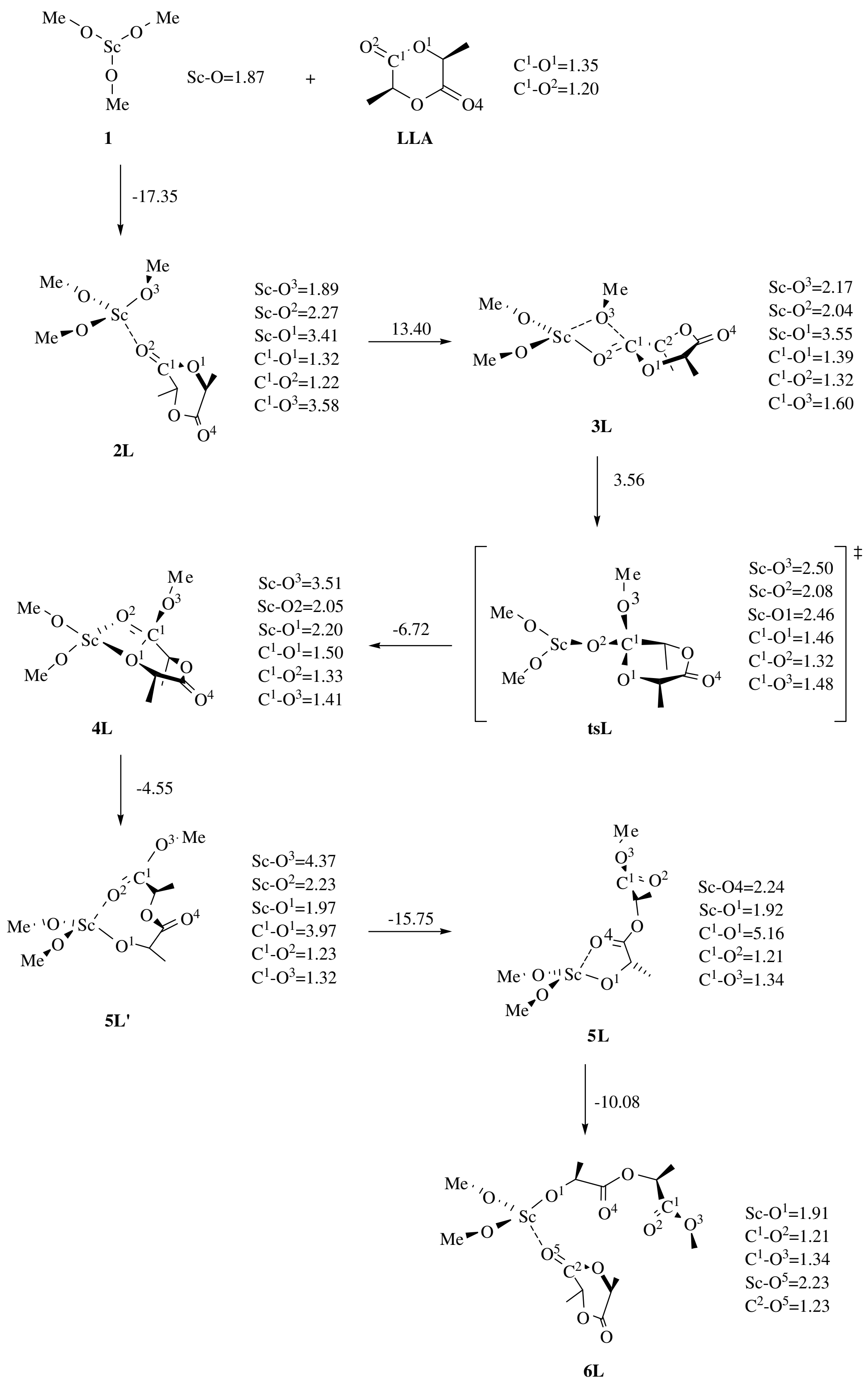


Fig. 5. ROP mechanism of LLA. Bond lengths are in Å and energies in kcal/mol.

The affinity between scandium and oxygen implies that tetrahydrofuran (THF) would be a good coordinating agent. Our calculations indicate a strong coordination (−21.56 kcal/mol) to Sc(OMe)$_3$ by THF (**1F**) (Fig. 3) which is close to that of CL (−22.08 kcal/mol). Thus, CL and other monomers are expected to compete with THF for the Sc center. This is consistent with other findings that TMC competes with THF for the Sm ion [40]. The calculated energies (PM3) of coordinative substitution of CL or LLA by THF have been reported as well [19,21] and agree qualitatively with the above.

The coordination of TMC onto Sc(OMe)$_3$ is somewhat different from the CL case as C^1 is flanked by oxygen on both sides. Like the case of CL, the DFT structure of **2T** indicates that the plane of the TMC ring is nearly vertical (90°) to that of the O atoms of the three methoxy groups (Fig. 4 and Fig. S5 in Supporting Information). However, the C^1–O^2 and Sc–O^3 bonds show a dihedral angle of 64.6° that is much larger than that for CL (11.2°). Also, the energy of coordination of TMC onto the Sc center is −20.14 kcal/mol, slightly smaller than that of CL (−22.08 kcal/mol). The addition of Sc–O^3 to the C^1–O^2 double bond transforms intermediate **2T** into **3T**. This involves rotation of the TMC ring around the C^1–O^2 bond that flattens the ring and decreases the dihedral angle of C^1–O^2–Sc–O^3 from 64.6 to 18.7°.

The transition state (**tsT**) in this case is analogous to **tsC** in that the displacement of the O^{3}Me group from the Sc center by the O^1 atom involves a slight rotation of the TMC ring around the C^1–O^2 bond. The next two steps are also similar. The energy barrier (energy difference between **2T** and **tsT**) is 20.69 kcal/mol which is close to that of CL (22.33 kcal/mol between **2C** and **tsC**), thus predicting similar initiation/polymerization rates.

The (*S*,*S*)-lactide (LLA) Sc complex (**2L**) has a virtually identical structure and conformation as the corresponding TMC complex showing a C^1–O^2–Sc–O^3 torsion angle of 47.2° (Fig. 5 and Fig. S6 in Supporting Information). However, the coordination of LLA to the Sc center is calculated as −17.35 kcal/mol, 4.73 kcal/mol *less* than that of the CL–Sc complex. Hence, LLA coordinates Sc more weakly than CL, TMC and THF. This may be due to the presence of the two inductively electron-withdrawing carbonyl groups in LLA. The subsequent mechanism is similar to that of CL and TMC. However, in contrast to **5L**′, the structure of **5L** differs from **5C** and **5T** in that a relatively stable five-membered ring is formed (Fig. 5). A coordination of this type was claimed to account for the stereoselectivity of *rac*-lactide polymerization initiated by Mg complexes [20].

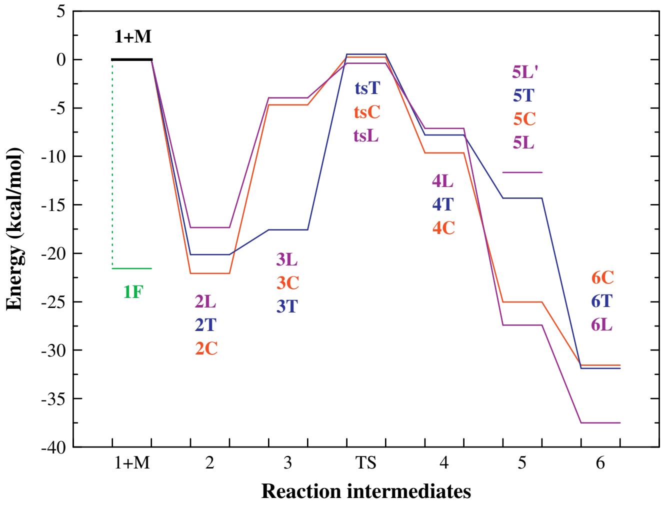


Fig. 6. Energy changes as a function of reaction progress for monomer addition for the polymerizations of CL (red), TMC (blue) and LLA (purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

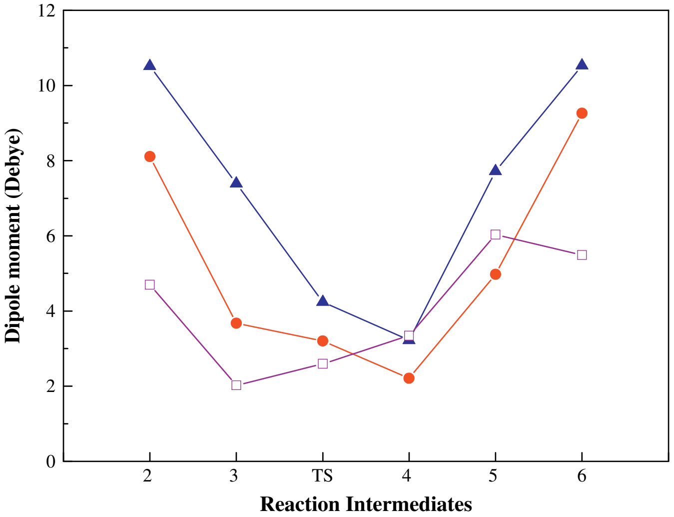


Fig. 7. Calculated dipole moments of reaction intermediates and transition states for monomer addition of CL (red), TMC (blue) and LLA (purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6 summarizes the energy changes of CL, TMC and LLA as a function of reaction progress. With similar geometries, intermediates **2** can be regarded as being equivalent to **6**. Thus, the above DFT based mechanisms may be applicable to both initiation and propagation. The energy of **5T** is close to that of **5L**′ but much higher than that of **5C** and **5L**. Assuming that the monomer coordination to Sc(OMe)$_3$ and that of **6C** are the same, the energies of intramolecular coordination of Sc by the chain carbonyl in **5C** can be evaluated as the difference between the energies of formation of **2C** and **6C**. This value was found to be −15.54 kcal/mol. The corresponding energies for TMC and LLA obtained by comparing the energies of formation of **6T** and **2T** and **6L** and **2L** are −2.56 and −7.27 kcal/mol respectively. The relatively weak intramolecular coordination for **5T** compared to **5C** and **5L** seems consistent with the presence of three sp^2 hybridized atoms in **5T**. The large decrease in energy in going from **5L**′ to **5L** (−15.75 kcal/mol) may be caused by the considerable ring strain in **5L**′ having four sp^2 hybridized atoms and the stability of the five-membered ring in **5L**. Overall, the large apparent energy change of LLA addition (between **1** and **6L**) (Fig. 6) may be due in part to the relaxation of the highly strained six-membered LLA ring containing two sp^2 hybridized carbon atoms, two sp^2 hybridized oxygens and two sp^3 carbons. The relatively stable structure of **6L** may explain the experimental fact that PCL active chain could initiate the ROP of LLA while PLLA could not initiate the ROP of CL [53].

The DFT based dipole moments (DM) of the intermediates are summarized in Fig. 7. In all three cases (CL, TMC and LLA) the DM values of **3**/**TS**/**4** are smaller than that of **2** and **6**. This distinguishes the coordination–insertion from the ionic mechanism. Hence these polymerizations are predicted and found to proceed more slowly in polar solvents [34,53,55]. Given the larger changes of the DMs of the CL and TMC monomers compared with LLA these effects should be most prominent for the case of CL and TMC. For the case of LLA the rate limiting step ***b*** (Scheme 2) would seem to predict the smallest polarity effects. To our knowledge these predictions remain to be tested.

4. Conclusions

DFT calculations of reaction intermediates in the ROP of CL, TMC and LLA initiated by Sc(OMe)$_3$ bring additional insight into the detailed mechanisms of their initiation and propagation processes. Transition states having penta-coordinated Sc are found in all cases and the apparent energy barriers of initiation (energy differences between **2** and the **TS**s) of CL, TMC and LLA are calculated as 22.3, 20.7 and 17.0 kcal/mol, respectively. THF is shown to coordinate the Sc center competitively with the monomers. The lower transition state dipole moments agree with the observed effects of solvent polarity on polymerization rates. Such studies may be applicable to yttrium and lanthanide initiators.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.06.006.

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